# Search and Characterization of Novel Superhard Phases in the B-C-N System Under Extreme Conditions

L. C. Ming, P. V. Zinin, and M. H. Manghnani, University of Hawaii, DMR-0102215

Novel high-pressure phase, cubic $BC_x$, ($8 \le x \le 10$), was synthesized at pressures 22-27 GPa and temperatures up to 2500 K by solid-state thermal decomposition of graphite-like BC using a laser-heated diamond anvil cell. The lattice parameter of the new phase at ambient conditions is 3.588(1) Å which is 0.6% larger than that of diamond. The effect of pressure on the volume of cubic $BC_x$ up to 52 GPa is shown in the Fig. 5. Using the two-parameter Birch Murnaghan equation of state to fit the data, we obtained values of bulk modulus $B_0$ = 335(4) GPa and its pressure derivative $B_0' = 4.5(3)$. The bulk modulus ($B_0$) of cubic $BC_x$ is smaller than those of diamond (442 GPa) and cBN (372 GPa), however, this phase still has one of the largest bulk moduli known for any solid. It is likely that the novel cubic $BC_x$ would have important industrial applications.

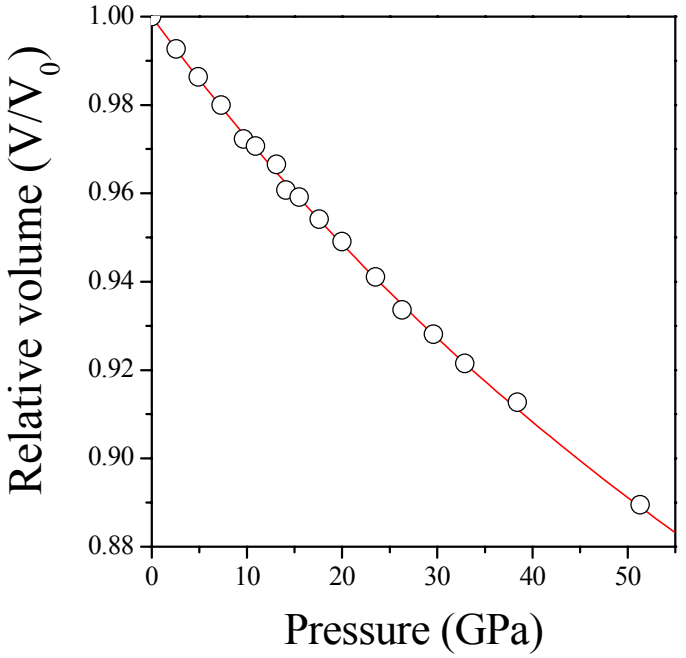


Fig. 1. The effect of pressure on the volume of $BC_x$ to 52 GPa at room temperature

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Liu and Cohen in 1989 first predicted theoretically that some denser forms of $C_3N_4$ such as the β-$C_3N_4$ phase should exhibit a bulk modulus and hardness higher than those of diamond because of the short length and high covalence of the C-N bond. Since then there has been much interest in studying the C-N system at high pressures and temperatures. In our recent study, we have subjected a turbostratic carbon nitride (t-CN) to 22 GPa (i.e., $2.2 \times 10^5$ atmospheres) and to 2250 K in a large-volume press. Based on the x-ray diffraction data from both quench and in *situ* experiments, a *P-T* phase diagram is proposed in Fig. 4. The fact that no β-$C_3N_4$ phase was obtained in this study suggests such a denser phase may only occur under a high nitrogen pressure so as to prevent the decomposition of the $C_3N_4$. Experiment in a diamond-anvil cell using nitrogen media is now in progress.

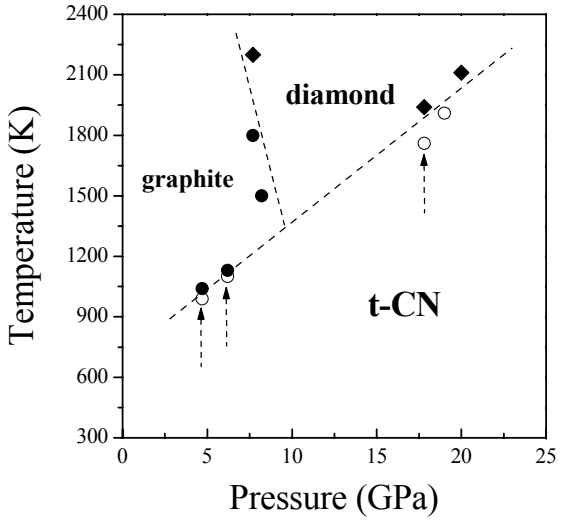


Fig. 2. A proposed *P-T* phase diagram for the turbostratic carbon nitride.

*J. Phys. Chem. Sol.* **64(**8) 1265-1270 (2003).

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Superhard diamond-like ternary B-C-N phases are highly desirable, as they might combine the best properties of the elemental or binary compounds of the system. For example, a diamond-cBN alloy should be more thermally stable and resistant to oxidation, less reactive with iron than pure diamond, and harder than cBN. Here we present nanostructure of the new $BC_2N$ phase obtained under high pressure and high temperature (Figure 3). The first Brillouin scattering measurements on nanocrystalline cubic phase of $BC_2N$ have been successfully performed using the "modified" platelet scattering geometry (Fig.4). We were able to measure both longitudinal (*Vp*) and shear (*Vs*) velocities independent of refractive index, and thus obtained values of 13.09±0.22 km/s and 8.41±0.14 km/s, respectively. Our results indicate the new nanocrystalline cubic $BC_2N$ phase is a new material with intriguing physical properties – while its hardness is higher than that of cBN, its velocities, and thus the bulk and shear moduli are all smaller than those of cBN.

*Phys. Rev. B* ***68****(5) 052104(3) (2003).*

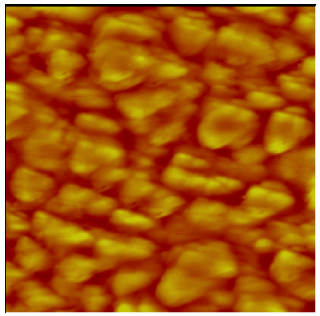

Fig. 3. Nanostructure of cubic $BC_2N$ nano-phase obtained by AFM image (tapping mode, scale 2 x 2 mm).

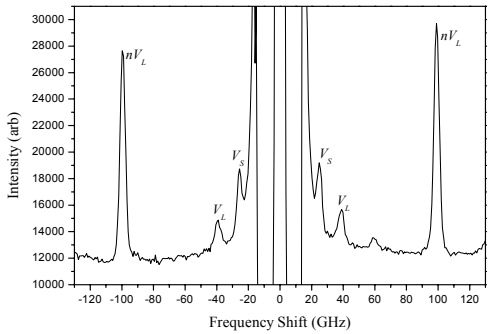


Fig. 4. Experimental BS spectrum ($\theta$ =50°) of nanocrystalline *c*-$BC_2N$.

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Raman measurements were conducted with the nanocrystalline cubic $BC_2N$ sample and gave us a mean Raman shift of 1325.7 $cm^{-1}$ (see Fig. 5). This position of the Raman band is located between the Raman peak of diamond (1332 $cm^{-1}$) and that of cubic $C_{0.3}(BN)_{0.7}$ (1323 $cm^{-1}$), showing the Raman shift decreases with decreasing the number of C atoms and is positively deviated from the straight line between the two end members (diamond and cBN at 1304 $cm^{-1}$). The large width of the observed 1325.7 $cm^{-1}$ most likely reflects random substitution of B and N atoms in the diamond lattice, which is also consistent with the cubic-$BC_2N$ being disorder as revealed from the synchrotron-based x-ray diffraction data.

*J. Raman Spectr. submitted* (2003).

**Education:**

Two graduate students (Sergey Tkachev,and Alexander Kurakevich) and a post-doctoral associate (Dr. V.L. Solozhenko) have made contributions to this research project.

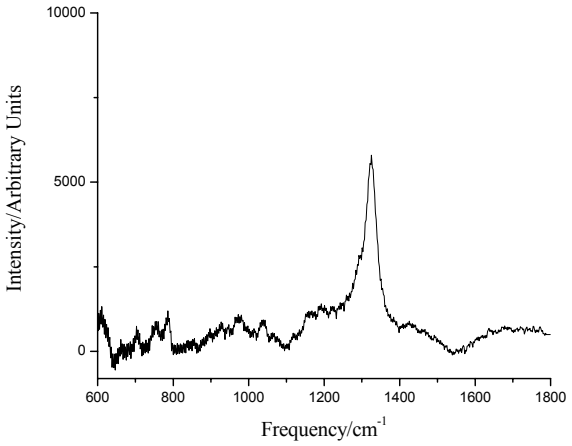


Fig. 5. Raman spectrum of the $BC_2N$ phase measured by UV laser .